



In re application of: ITOH, Muneharu

Group Art Unit:1756

Serial No.: 10/721,069

Examiner: DOTE, JANIS L.

Filed November 26, 2003

P.T.O. Confirmation No.:7768

**For: TONER AND IMAGE-FORMING METHOD THEREWITH**

**DECLARATION UNDER 37 CFR1.132**

Commissioner for Patents  
P.O.Box 1450  
Alexandria, VA 22313-1450

February 21, 2006

Sir:

I, **Muneharu ITOH**, a citizen of Japan, hereby declare and state:

1. I have a degree in Electronic Chemistry which was conferred upon me by Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology in Yokohama, Japan, in 2001.

2. I have been employed by ZEON CORPORATION since 2001 and I have had a total of 5 years work and research experience in Chemistry.

3. I, under my direct supervision and control, have conducted the following experiment:

The undersigned declares that all statements made herein of his/her own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed this 21 day of 2, 2006

Muneharu Itoh  
Muneharu ITOH



## EXPERIMENT

### Manufacturing Example 1

24 parts (parts by weight, hereinafter the same) of methyl ethyl ketone and 6 parts of methanol were dispersed in 100 parts of a resin-base negative-charge control agent (FCA626N: trade name of a product of Fujikura Kasei Co., Ltd., a monomer unit having a sulfonic acid group: 7 % by weight), and the resultant mixture was mixed by rolls under cooling. When the mixture wound on the rolls, 100 parts of a magenta pigment (C. I. pigment red 122: a product of Clariant Co., Ltd.) was gradually added to the mixture. The resultant mixture was further mixed for an hour to prepare a negative-charge control resin composition 1. During this period, the clearance between the rolls was initially 1 mm, broadened gradually, to finally to 3 mm, and an organic solvent (a solvent mixture of methyl ethyl ketone /methanol = 4/1) was added occasionally according to mixing and kneading condition of the charge control resin composition. After the stirring, the organic solvent added was removed under reduced pressure.

### Manufacturing Example 2

A negative-charge control resin composition 2 was prepared as in Manufacturing Example 1 except that C. I. pigment red 185 (a product of Clariant Co., Ltd.) was used as a magenta pigment.

### Toner-Manufacturing Example 1

A polymerizable monomer mixture for core consisting of 89 parts of styrene, 11 parts of n-butyl acrylate, 0.725 parts of divinylbenzene, and 0.25 parts of a polymethacrylic ester macromonomer ("AA6", Trade Name, manufactured by Toagosei Chemical Industry Co., Ltd.); 8 parts of the above-mentioned negative-charge control resin composition 1; and 10 parts of dipentaerythritol hexamyrystate were mixed and agitated so as to be uniformly dispersed; thus, a polymerizable monomer composition for core was obtained.

At the same time, an aqueous solution containing 6.6 parts of sodium hydroxide (alkali metal hydroxide) dissolved in 50 parts of ion-exchanged water was gradually added to an aqueous solution containing 10.8 parts of magnesium chloride (water-soluble polyvalent metallic salt) dissolved in 250 parts of ion-exchanged water, with stirring, to prepare a magnesium hydroxide colloidal dispersion (colloid of hardly water-soluble metal hydroxide).

Additionally, 1 part of methyl methacrylate and 65 parts of water were subjected to a finely dispersing treatment using an ultrasonic emulsifier to obtain an aqueous dispersion of a polymerizable monomer for shell.

The above-mentioned polymerizable monomer composition for core was poured into the aqueous dispersion containing magnesium hydroxide colloid, and the resultant mixture was stirred until droplets stabilized.

Then, to the mixture, 1 part of triisobutyl mercaptan (a product of Bayer A.G.), 1 part of tetraethyl thiuram disulfide (a product of Ouchi Shinko Chemical Industrial Co., Ltd.), and 5 parts of t-butyl peroxy-2-ethylhexanoate ("PERBUTYL O", Trade Name, manufactured by NOF CORPORATION) were added. Then, the resultant dispersion was stirred under high shearing force at 15,000 rpm for 30 minutes by means of an Ebara Milder ("MDN303V", Trade Name, manufactured by Ebara Corporation) to generate finer droplets of the polymerizable monomer composition for core. The thus-formed aqueous dispersion containing the polymerizable monomer composition mixture was charged into a reactor vessel equipped with an agitating blade, and heated so that a temperature was controlled at 90°C to initiate a polymerization reaction. At the time when the conversion of the monomer into a polymer reached almost 100%, an aqueous dispersion of the polymerizable monomer for shell and 0.2 parts of water-soluble polymerization initiator ("VA-086", Trade Name, manufactured by Wako Pure Chemical Industries, Ltd.,) (2,2'-azobis-(2-methyl-N-(2-hydroxyethyl))propionamide) dissolved in 65 parts of distilled water were charged into the reactor vessel. After the polymerization reaction for 8 hours, the reaction was stopped to obtain an aqueous dispersion containing core-shell structured colored particles having a pH of 9.5.

Thus obtained dispersion including the core-shell structure colored polymer particle was: washed with acid (at 25 °C for 10 minutes) by controlling pH thereof not larger than 6 with sulfuric acid while stirring; dehydrated by filtration; and washed with water after generating slurry again by adding 500 parts of ion exchanged water. Then, after the solid content was dehydrated and washed by water for several times, it was separated by filtration and dried at 45 °C for 2 days and nights with a drier, core-shell structured colored particles for toner were obtained.

100 parts of thus obtained colored polymer, 1.0 part cube shaped calcium carbonate with volume average particle diameter of 0.3  $\mu\text{m}$  (trade name: CUBE-03BHS, product of Maruo Calcium Co., Ltd.), 0.5 part of fine silica particle with volume average particle diameter of 12 nm (trade name: RX-200, product of Nippon Aerosil Co., Ltd.) and 2.0 parts of fine silica particle with volume average particle diameter of 40 nm (trade name: RX-50, product of Nippon Aerosil Co., Ltd.) were mixed at 1,400 rpm for 10 minutes with a Henschel mixer to obtain a toner 1.

#### Toner-Manufacturing Example 2

A toner 2 was obtained as in Toner-Manufacturing Example 1 except that 1 part of methyl methacrylate and 0.5 parts of diethylaminoethyl methacrylate (“LIGHT-ESTER DE” trade name of a product of Kyoeisha Chemical Co., Ltd.) were used as the polymerizable monomer for shell.

### Toner-Manufacturing Example 3

A toner 3 was obtained as in Toner-Manufacturing Example 1 except that 1 part of methyl methacrylate and 1 part of diethylaminoethyl methacrylate (“LIGHT-ESTER DE” trade name of a product of Kyoeisha Chemical Co., Ltd.) were used as the polymerizable monomer for shell.

### Toner-Manufacturing Example 4

A toner 4 was obtained as in Toner-Manufacturing Example 1 except that 2 parts of the negative-charge control resin composition 1 prepared in Manufacturing Example 1 and 1 part of the negative-charge control resin composition 2 prepared in Manufacturing Example 2 were used.

### Toner-Manufacturing Example 5

A toner 5 was obtained as in Toner-Manufacturing Example 1 except that 12 parts of the negative-charge control resin composition 1 prepared in Manufacturing Example 1 and 6 parts of the negative-charge control resin composition 2 prepared in Manufacturing Example 2 were used.

### Measurement of Charge Amount of Toner

#### (1) Measurement of charge amount by a suction method

A toner was set to a commercially available non-magnetic-one-component developing type printer with a resolution of 600 dpi (Microline 3010C: trade name of a

product of Oki Data Corporation) and was left to stand overnight at a temperature of 23°C and a humidity of 50% (under N/N conditions). Then, 5 sheets were printed at a printing density of 5 %. The toner on a developing roll of the printer was sucked with a suction-type charge amount measuring apparatus (210HS-2A: trade name of a product of Trek Japan Co., Ltd.) to measure the charge amount. From the obtained charge amount and the weight of the sucked toner, the charge amount per unit weight was determined.

(2) Measurement of charge amount by a blow-off method

A carrier (59.7 g, TEFV150/250: trade name of a product of Powder Tech Co., Ltd.) and a toner (0.3 g) were weighed and put into a SUS pot with a volume of 200 ml. The pot was rotated at 150 rpm for 30 minutes to apply frictional electrification to fine silica particles in the toner. The charge amount was measured by blowing the carrier and the fine silica particles by nitrogen gas with a pressure of 1 kg/cm<sup>2</sup> using a blow-off meter (TB-200: trade name of a product of Toshiba Chemical Corporation).



## Results

	(1) Charge Amount measured by the suction method ( $\mu\text{Q/g}$ )	(2) Charge Amount measured by the blow-off method ( $\mu\text{Q/g}$ )
Toner 1	-63	-113
Toner 2	-67	-107
Toner 3	-55	-112
Toner 4	-59	-121
Toner 5	-60	-110